

REMARKS

The Official Action of March 24, 2005 has been carefully considered and reconsideration of the application as amended is respectfully requested.

Applicants submit herewith certified copies of each of the priority applications, CN03105214.2 (02/24/2003) and CN03153662.X (08/20/2003).

Claims 1, 4, 13, 20 and 21 have been amended to clarify that the recited silica material comprises particles that are necessarily present in the claimed composite carrier. The positive recitation of silica particles precludes the possibility that they have a particle size of zero. Accordingly, it is respectfully requested that the Examiner withdraw the rejections to the claims on the basis that the silica particles could allegedly be omitted.

Claims 11, 15 and 25 have been amended to remove the bases for the rejections to these claims under 35 USC 112, second paragraph. The ratios recited in claim 25 would have been clear to one of skill in the art from the ratios recited in the original claims, especially since the external electron donor component is recited in the original claims as being optional (see original claim 22) such that its comparative value could be zero.

Claims 20, 21 and 22 have been amended to remove the bases for the objections to these claims at page 2 of the Official Action. With specific respect to the objection to claim 22, the claim as amended does not recite any method and recites only one reaction product.

With respect to the rejections to claims 7 and 8, Applicants respectfully note that these claims recite the average particle size of **the spheric particles** of the composite carrier and not the average particle size of **the silica material**, which is only one component of the composite carrier. Accordingly, Applicants respectfully request withdrawal of the rejection to these claims. All claims as amended are respectfully believed to satisfy the dictates of 35 USC 112, second paragraph.

New claims 26 and 27 have been added more completely to define the subject matter which Applicants regard as their invention. These claims are product-by-process claims which use the "consisting essentially of" transitional to limit the scope of the claimed invention to products formed by the specified steps "and those that do not materially affect the basic and novel characteristic(s)" of the claimed invention (see MPEP Section 2111.03). As discussed below, the cited art teaches steps which would materially affect the basic and novel characteristics of the catalyst carrier and catalyst component claimed in claims 26 and 27 respectively and thereby teach away from the invention defined in these claims.

Claims 1-25 stand rejected under 35 USC 103(a) as allegedly being unpatentable over Spencer et al in view of Morini et al. Applicants respectfully traverse this rejection.

The claimed invention is based in part upon Applicants' discovery that a composite catalyst carrier comprising magnesium halide and particles of a silica material having an average particle size of less than 10 microns provides advantageous effects when used in a catalyst for

propylene polymerization. In particular, as discussed in the specification at page 6, first paragraph, when used in propylene polymerization, the catalysts according to the claimed invention exhibit high activity and high stereospecificity. Moreover, as shown by comparing the Examples on pages 20-32 of the specification with the Comparative Example on pages 32-33, a catalyst prepared by reacting the recited magnesium halide and titanium compounds, wherein the magnesium halide is **not** present as part of a composite carrier as claimed, produces polymers having a narrower molecular weight distribution than those produced with the claimed invention.

More particularly, the catalyst component for propylene polymerization according to the claimed invention comprises reaction product of a composite carrier, which is prepared first and comprises magnesium halide and a silica material with an average particle size of greater than 0 and less than 10 microns, with a titanium compound and an internal electron donor compound. As indicated in the specification at page 19, line 22 to page 20, line 9, the catalyst component of the invention exhibits many advantages. In particular, it can be seen from the comparison of Examples and Comparative Example 1 that polymer obtained by using the catalyst of the claimed invention has a broader molecular weight distribution with Mw/Mn being larger than 7, which would provide better processibility of the polymer, while polymer obtained by using a catalyst, which is prepared by employing 1,3-diether compound as internal electron donor yet no composite carrier of the claimed invention, would have a narrower molecular weight distribution (see specification at page 33, lines 17-28).

All claims as presently on file recite a **composite catalyst carrier**, which by definition requires that the recited magnesium halide and silica material be present as part of the catalyst carrier (support) of a catalyst component. Moreover, the product-by-process claims all require that the composite catalyst carrier be prepared by a process which includes a drying step, wherein the formation of the composite catalyst carrier is completed with the drying step prior to any reaction between the composite catalyst carrier and, for example, a titanium compound to form a catalyst component for propylene polymerization. As is well known in the art, the properties of a catalyst are determined by the method of its preparation (see page 225 of Kirk-Othmer Concise Encyclopedia of Chemical Technology, submitted herewith, and the Morini et al reference cited by the Examiner). Accordingly, one of skill in the art could not reasonably expect that a catalyst prepared by a process that does not comprise separate formation of a composite catalyst carrier from the recited components would have the same properties as a catalyst formed by the claimed process even if the components of the catalyst were the same.

The primary reference cited by the Examiner, Spencer et al, discloses a supported transition metal containing catalyst component comprising the product resulting from contacting (1) a solid, porous inorganic oxide support material selected from the group consisting of silica, alumina, or a combination of silica and alumina; (2) a hydrocarbon soluble organomagnesium alkoxide or dialkoxide; (3) a titanium compound; optionally, (4) a vanadium compound; and (5) a Group IIIA metal alkyl halide. Spencer, et al. neither disclose a composite carrier comprising magnesium halide and silica material nor the catalyst of the claimed invention comprising such composite carrier.

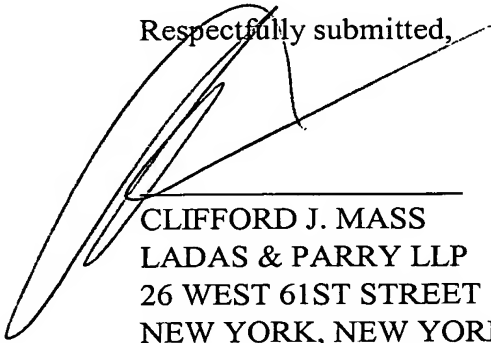
Morini et al. (US 5,723,400) disclose a process for the preparation of a solid catalyst component, comprising reacting a magnesium halide, or a magnesium halide precursor, with a titanium compound and an electron donor compound. Morini et al. have found that, if in the preparation of the solid catalyst components one makes at least two successive electron-donor additions in the proper order, one obtains solid catalyst components capable of conferring to the catalyst obtained from them an improved activity/stereospecificity balance in the polymerization of olefins (see Morini et al at col.1, lines 32-38). Again, Morini et al. neither disclose a composite carrier comprising magnesium halide and silica material nor the catalyst of the claimed invention comprising such composite catalyst.

Since neither of the cited references shows or suggests the process of preparation of a catalyst comprising the separate formation of a composite catalyst carrier comprising the recited components prior to reaction of the catalyst carrier with, for example, a titanium compound to form a catalyst component, the references cannot be said to teach the features of the claimed invention, either alone or in combination (even assuming for the sake of argument that such combination were proper, see below). In particular, those of skill in the art could not expect a catalyst formed by a combination of Spencer et al and Morini et al to have the same properties as the claimed catalyst, which is formed by a different process and can be used to prepare a polypropylene having broad molecular weight distribution. In this respect, Applicants respectfully note that the polymer described by Spencer et al has a Mw/Mn ratio of, for example, less than about 3.6 and Morini et al is silent on this issue.

In view of the above, and the failure of the references to show or suggest the claimed composite catalyst carrier, it is respectfully submitted that the references would not show all features of the claimed invention even if they were properly combinable, and the references do not set forth a *prima facie* case of obviousness for this reason alone (see MPEP Section 706.02(j)). Moreover, it is respectfully submitted that the references are not properly combinable and do not set forth a *prima facie* case of obviousness for that reason as well (Id.). In this respect, Spencer et al describes a **supported** catalyst prepared in the described manner and Morini et al describes an **unsupported** catalyst prepared in a different manner. In view of the distinctions recognized in the art between these supported and unsupported catalysts, and the teaching in Morini et al as to the criticality of the method of preparation of the catalyst component described therein, there respectfully would have been no motivation absent the hindsight provided by the present specification to combine the cited references in the manner proposed by the Examiner. This is *a fortiori* true with respect to claims 26 and 27, which preclude preparation of a slurry of a silica support, magnesium compound and titanium compound prior to any drying step (see Spencer et al at column 4, line 39 to column 5, line 3; and the Examples beginning in the reference at column 20). Accordingly, it is respectfully submitted that the references do not set forth even a *prima facie* case of obviousness for the invention as claimed.

In view of the above, it is respectfully submitted that all rejections and objections of record have been overcome and that the application is now in allowable form. An early notice of allowance is earnestly solicited and is believed to be fully warranted.

Respectfully submitted,

A large, stylized handwritten signature in black ink, appearing to read 'Clifford J. Mass', is written over the signature line and extends upwards and to the left.

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tangantangan oil, and Neoloid. The oil is a triglyceride of fatty acids which contains 87–90% ricinoleic acid, *cis*-12-hydroxyoctadec-9-enoic acid, $\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{OH})\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$, a rare source of an eighteen carbon hydroxylated fatty acid with one double bond. The oil is pale, yellow, and viscous, with a slightly characteristic odor, and nearly tasteless but familiarly unpleasant through its minor use as a purgative.

Recovery of castor oil from castor beans is commonly by the use of hydraulic pressers or expellers followed by solvent extraction (see Vegetable oils).

Properties

The average fatty acid composition of castor oil contains ricinoleic acid (89.5%), dihydroxystearic acid (0.7%), palmitic acid (1.0%), stearic acid (1.0%), oleic acid (3.0%), linoleic acid (4.2%), linolenic acid (0.3%), and eicosanoic acid (0.3%).

The oil is distinguished from other triglycerides by its high specific gravity (0.957–0.961 at 25/25°C), viscosity = (6.5–8.0) cm^2/s hydroxyl value (160–168) and its solubility in alcohol (1:2 in 95% ethanol at 20°C); it is soluble in polar organic solvents, less soluble in aliphatic hydrocarbon solvents, and slightly soluble in petroleum ether.

Chemical Modification

Castor oil serves as an industrial raw material for the manufacture of a number of complex derivatives.

Catalytic dehydration uses as catalysts sulfuric acid and its acid salts, oxides, and activated clay at 230–280°C. This converts castor oil to an excellent drying oil called dehydrated castor oil (see Driers and metallic soaps), used extensively by the coatings industry. In a typical process, castor oil is heated to 230–280°C under vacuum and 3–5% diluted sulfuric acid is added to it at a controlled rate.

In sulfonation, concentrated sulfuric acid is added over a period of several hours while cooling to maintain a temperature of 25–30°C, followed by washing to remove surplus acid, and then neutralized to produce sulfonated castor oil, also known as Turkey red oil. Commercial sulfated castor oil contains ca 8.0–8.5% combined SO_3 ; the sulfate group imparts excellent wetting, emulsification, and dispersing characteristics. Sulfonation with anhydrous SO_3 (2 mol) at temperatures higher than the sulfuric acid treatment produces a product with better hydrolytic stability and contains less inorganic salts and free fatty acids.

Alkali fusion yields two different sets of products, depending on the reaction conditions. At 180–200°C using one mole of sodium or potassium hydroxide, methyl hexyl ketone and 10-hydroxydecanoic acid result. Two moles of alkali per mole of ricinoleate at 250–275°C and a shorter reaction cycle produce 2-octanol and sebacic acid.

Oxidation produces clear viscous oils resulting from controlled oxidation by intimate mixing (blowing) of castor oil at 80–130°C with air or oxygen with or without the use of a catalyst. The reaction is promoted by transition metals and the properties of the oil are dependent on the reaction conditions.

Pyrolytic decomposition at 340–400°C splits the ricinoleate molecule at the hydroxyl group to form heptaldehyde and undecylenic acids. Heptaldehyde is converted to heptanoic acid by oxidation techniques, and to heptyl alcohol by catalytic hydrogenation.

Hydrogenation can be performed in a number of ways to produce unique derivatives. For example, simple double-bond hydrogenation at 140°C in the presence of Raney nickel catalyst produces glyceryl tris(12-hydroxystearate), mp 86°C. Hydrogenation of ricinoleic acid with a copper cadmium catalyst at 220°C and 26 MPa (ca 250 atm) yields 70% ricinoleyl alcohol. Stearates are prepared by dehydrating hydrogenated castor oil, or by dehydration of castor oil followed by full hydrogenation of the diene intermediate. The hardness, flexibility, mp, and iodine value of the finished products are controlled by the degree of hydrogenation. Esters of castor oil are changed by hydrogenation from fluid products to soft waxes with a mp range of 45–65°C.

Alkoxylation with ethylene oxide produces ethoxylated derivatives with varied degrees of hydrophobic–hydrophilic properties, and with propylene oxide yields mineral oil soluble derivatives. The reaction is

carried out at 120–180°C and 0–405 kPa (0–4 atm) using alkaline catalysts.

In the production of nylon-11, castor oil is transesterified with methyl alcohol to form glycerol and methyl ricinoleate, which undergoes pyrolysis at ca 450–500°C to form methyl 10-undecylenate and heptaldehyde. Rilsan monomer is formed by addition of bromide and then heated to give the polymer by condensation. Nylon-11 has a mp range of 186–190°C which facilitates high speed, uniform processing. It displays excellent chemical resistance and stability in contact with all types of fuels, along with shock and vibration resistance.

Uses. Castor oil is sometimes used as a purgative, but is primarily used as a raw material for the preparation of chemical derivatives used in coatings; urethane derivatives (see Urethane polymers); surfactants (qv) and dispersants; cosmetics; and lubricants. Nylon-11 is used in the automotive industry, in powder coatings (qv), or coatings that require no solvents.

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F.C. Naughton, *J. Am. Oil Chem. Soc.* 51, 65 (1974).

K.T. Achaya, *J. Am. Oil Chem. Soc.* 48, 759 (1971).

M. Brauer and R. Sabia, "Design Consideration, Chemistry and Performance of a Reenterable Polyurethane Encapsulant," *International Wire and Cable Symposium Proceedings*, U.S. Army Electronics Command, Washington, D.C., Nov. 1975, pp. 104–111.

CATALYSIS

A catalyst is a substance that alters the velocity of a chemical reaction without appearing in the products. Catalysts accelerate reactions but do not change equilibria; both forward and backward reactions are catalyzed to the same extent. Increasing the velocity of a desired reaction relative to unwanted reactions maximizes the formation of a desired product.

Catalysts are believed to function through an unstable chemical complex formed between the catalyst and reactant molecules. This complex reacts to produce new compounds with dissociation of the complex and regeneration of the catalyst which can then bring about the transformation of additional reactant molecules (see Enzymes).

Chemical and Physical Aspects

The rate of a chemical reaction is proportional to a rate constant:

$$k = Ae^{-E/RT}$$

Because of the exponential form of the equation, even a small decrease in E , the activation energy, can bring about a large increase in velocity. The catalytic pathway is a series of three chemical reactions: formation of the complex (activated adsorption), surface reaction, and desorption.

Solid surface catalysts invariably adsorb reactant molecules, adsorption and chemical reaction occurring on active centers identified as certain types of lattice defects. The geometric factor in catalysis emphasizes the significance of the reactant molecule's spacial arrangement and the catalyst crystalline lattice.

The activity and selectivity of a catalyst are affected by its pore structure, eg, in a very slow reaction molecules can diffuse through a pore system to the center of a catalyst particle before they react and the entire internal surface area will be used. The fraction of surface available in a given reaction can be calculated. The experimental rate constant, K_{exp} , is compared with

$$K_d = (18/a^2)\rho BVgD$$

where a = catalyst granule size, ρB = bulk density, Vg = porosity, and D = diffusion constant.

Various theories have been applied to catalysis, including quantum mechanical treatment of solids and the electron band, crystal field, resonance valence bond, and molecular orbital ligand field theories.

Techniques

The following factors are considered when choosing a catalyst for a specific reaction: selectivity, or the efficiency in catalyzing a desired transformation; activity, or the overall conversion, expressed as the amount of reactant in contact with the catalyst under a given set of conditions converted to all products; stability, the ability to retain initial activity and selectivity over the catalyst's lifetime; physical suitability; regenerability; and cost.

Heterogeneous catalysts, in contrast to homogeneous catalysts, form a separate phase from reactants and products and are usually solids. They have a microporous structure and a very large internal surface area (it may reach 1000 m²/g) but these colloidal catalysts are often inactivated by the presence of small amounts of poisons. Poisons act by combining with an active site in the catalyst surface and rendering it inactive.

Most poisons are strongly sorbed and react quantitatively with active sites to form stable inactive surface compounds, eg, acidic catalysts are poisoned by basic nitrogen and alkali-metal ions, metal catalysts by sulfides, arsenic and lead compounds. Some poisons cause loss of selectivity, eg, nickel and copper present in gas oils used in catalytic cracking. In some cases, poisons minimize a desired reaction while permitting an undesired reaction. Reactivation of a catalyst is sometimes accomplished by decomposition or desorption of the poison.

In contrast, small amounts of promoters or cocatalysts may cause striking increases in catalytic activity.

In industrial use, catalysts lose activity and sometimes selectivity. In general, heterogeneous catalysts lose effectiveness owing to overheating and contamination. Contaminants affecting catalytic efficiency are metals entrained in feedstocks; oxygen, nitrogen, or sulfur compounds; and polynuclear aromatic compounds which form coke.

Preparation

Properties of a catalyst are determined by its preparation, with care taken to ensure duplication of characteristics. Colloid chemistry is important, including gel preparation (eg, hydrous oxides and systems mainly of silica or alumina are amenable to gel formation), leaching selected components from solids (eg, Raney nickel catalyst is prepared by leaching aluminum from a nickel-aluminum alloy by means of a caustic alkali), or decomposition of salts or hydrates with gas evolution. Frequently, the support is manufactured first by one of these techniques followed by impregnation with additional chemical components. The product may again require suitable treatment, eg, precipitation, calcination, reduction (eg, for hydrogenation catalysts such as nickel, cobalt, iron, or copper catalysts), etc.

Organic and Inorganic Chemicals

Important catalytic commercial processes include the Deacon process; platinum-catalyzed oxidation of ammonia for nitric acid production; the Haber and Mittasch ammonia synthesis process; hydrogen production employing catalytic reactions such as reforming, shift, and methanation; hydrogenation techniques for hardening fat; synthesis of methanol from carbon monoxide and hydrogen; production of phthalic anhydride via oxidation of naphthalene; oxo reaction to produce aldehydes, which can be catalytically hydrogenated to the corresponding alcohols; catalytic dehydrogenation of butene or butane (see Butadiene); the catalytic cracking, reforming, or hydrosulfurization of petroleum; polymerization for production of plastics and synthetic rubber; the production of polyurethane plastics.

Transition-Metal Complexes — Homogeneous Catalysis

The distinction between homogeneous and heterogeneous catalysts has been disappearing as fundamental similarities have been recognized. However, certain transition-metal complexes are classified as homo-

geneous catalysts since they can be molecularly dispersed in solution, eg, hydrocobalt tetracarbonyl, HCo(CO)₄. Some homogeneously catalyzed reactions are hydrogenation, hydroformylation, double-bond migration, polymerization, and oxidation.

Organometallic complex catalysts tend to be highly active, specific, and selective, and may resist poisoning better than heterogeneous systems. The catalytic center may have two metal sites. Organometallic catalysts have a central transition-metal atom or ion bonded to molecules known as ligands which form a polyhedron around the metal. The nature of the metal and ligands critically influences the electronic structure of the complex. The coordination bonding properties of the metal are a key feature of the catalytic complexes. Important reactions of catalyst complexes are ligand exchange, oxidative addition, and the insertion reaction.

The most important industrial reactions are the Wacker process (see Acetaldehyde); vinyl acetate (see Acetic acid; Vinyl polymers) the oxo process (see Oxo process); methanol carbonylation (see Acetic acid); and the Ziegler-Natta polymerizations (see Olefin polymers).

The advantage of complex catalysts including the anchored complexes lies in the predictability of their properties, the ease of interpreting reaction mechanisms, and the consequent potential for extending the homogeneous catalysts to many new applications.

Oxidation Catalysis

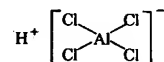
Classical examples of heterogeneous catalysis include oxidation of CO over copper, of NH₃ over Pt, and of SO₂ over Pt or V₂O₅. Heterogeneous oxidation catalysis is similar to catalysis by metal complexes since both utilize a metal of variable valence.

Commercially important hydrocarbon-oxidation processes include oxidation of benzene to maleic anhydride and toluene to benzoic acid, naphthalene and xylenes to phthalic acids, ethylene and propylene to their respective epoxides (see Hydrocarbon oxidation). The catalytic ammoxidation of propylene, eg, the Sohio process, is the successful process for the manufacture of acrylonitrile (see Acrylonitrile). Ethylene dichloride, the precursor of vinyl chloride, is manufactured by the oxidation of ethylene (see Chlorocarbons; Vinyl polymers).

Catalysis Applied to Fuels

The concepts of acid and basic catalysis, as proposed by Brønsted and Lowry, apply to reactions of industrial importance, particularly hydrocarbon reactions used in large-scale petroleum refining.

Acid catalysts are employed in such diverse areas as Friedel-Crafts reactions (qv) and reactions in the presence of clays. The isomerization of *n*-butane over an aluminum halide-hydrogen catalyst takes place only in the presence of olefins. Friedel-Crafts catalysts, mineral acids, such as H₂SO₄ and HF, and claylike substances, eg, H₂O-Al₂O₃-SiO₂, all act in a similar manner because of their essential acidity. In each case the active catalyst contains a proton; it is a Brønsted acid. For example, hydrogen chloride plus aluminum trichloride give



Catalytic activity of acid catalysts is correlated with surface acidity for different reactions. The Brønsted acidity is necessary for successful catalytic cracking, and the distribution of acid strengths is important.

Basic catalysts are employed less than acid catalysts, but are used industrially for polymerization of conjugated dienes as well as for the isomerization of olefins, dehydrogenation of certain diolefinic materials to aromatics, alkylation of arylalkanes, and polymerization of mono-olefins. Base catalysis gives different products than acid catalysis, eg, ethylene alkylates toluene in the side-chain with a base catalyst whereas acid catalysis gives ring alkylation.

Zeolites (Molecular Sieves)

Crystalline zeolites are silicates with an open framework, regular structure, and apertures of molecular dimensions based on a tetrahedron

of four oxygen ions surrounding a smaller silicon or aluminum ion (see Molecular sieves). Important zeolite catalysts are known as X, Y (similar to the rare natural mineral, faujasite), erionite, and mordenite, and the newer ZSM-5 and ZSM-11. The most significant application of crystalline zeolites has been in catalytic cracking where catalysts containing 10-20% zeolites greatly improve selectivity and activity.

Dual-Function Catalysts

Reforming represented a significant advance in the utilization of the dual-function catalysts, eg, reforming with platinum catalysts is today the second largest industrial catalytic application (see Petroleum). Another example of dual functionality is the conversion of C_6 -cycloparaffins (cyclohexane and methylcyclopentane) over single- and dual-function catalysts for converting methylcyclopentane to benzene. For certain reactions, dual-function catalysts can accomplish more than passing the reactants through two reactors in sequence, each filled with a different single-function catalyst.

Multimetallic Catalysis

Bimetallic cluster catalysts are composed of atoms of two different metals in a state of high dispersion on a carrier. Dispersion refers to the fraction of atoms in a metal crystallite that exist on the surface, with the degree of dispersion increasing with decreasing crystallite size. These novel bimetallic systems offer a new range of catalytic properties and are not limited to combinations of metals that form bulk alloys. New metallic catalysts with high activity and unprecedented activity maintenance are employed in the reforming of petroleum naphthas to high-octane gasoline and in isomerization, hydrocracking, and hydrogenation. In the petrochemicals field, improved Pd-Au catalysts are utilized for the synthesis of vinyl acetate, whereas more selective catalysts (eg, Ag-Au, Cu-Au) are used for the partial oxidation of olefins. Bimetallic catalysts show increased activity, improved resistance to poisoning by coke accumulation or deposition, and optimize product selectivity, eg, dehydrocyclization and aromatic hydrogenation are possible with a minimum of cracking reactions (hydrogenolysis) while maintaining very high hydrogenation activity.

Synthetic Fuels

Synthetic fuels from coal, oil shale, and biomass are expected to become of enormous industrial importance with catalysis playing a key role in the conversion of these complex solids to more convenient gaseous and liquid forms, and in the removal of sulfur, nitrogen, and oxygen in addition to inorganic mineral matter (see Fuels, synthetic).

Four general types of coal liquefaction processes are catalytic hydroliquefaction, pyrolysis, solvent extraction, and indirect synthesis (Fischer-Tropsch). The mechanism of direct coal liquefaction is believed to consist of a primary thermal pyrolysis of coal, followed by catalytic hydrogenation of the reactive fragments or asphaltenes formed by pyrolysis. Several direct catalytic coal-hydroliquefaction processes use active cobalt-molybdenum-alumina catalysts developed for petroleum desulfurization, including the H-Coal process (HRI), Synthoil (DOE), SRC and EDS (Exxon), and CCL (Gulf Oil), with others being researched.

In contrast to direct coal hydroliquefaction, in indirect liquefaction coal is gasified to a mixture of $CO + H_2$, followed by catalytic conversion to fuel products (Fischer-Tropsch process). The influence of the catalyst is profound, product distribution obtained varies considerably (see Table 1). The SASOL process is in commercial operation in South Africa. A plant using the Mobil process is being built in New Zealand.

Catalysis is effective in all three reactions involved in coal gasification, ie, gasification, shift, and synthesis.

Methanation is used commercially to convert relatively small amounts of harmful carbon oxides to CH_4 , where, as in ammonia synthesis, CO would especially interfere with catalytic conversions of gas mixtures. Methanation also will be used on a large scale in the manufacture of high heat values or pipeline gas, essentially methane.

Chemicals are expected to be derived from the refining of coal hydroliquefaction, especially aromatics, or from gas synthesis.

Table 1. Syngas Process Products

Product	Process, % of product		
	SASOL-I		
	Fixed	Fluid	Mobil
light gas C_1, C_2	7.6	20.0	1.3
LPG C_3, C_4	10.0	23.0	17.8
gasoline C_5-C_{12}	22.5	39.0	80.9
diesel $C_{13}-C_{18}$	15.0	5.0	0
heavy oil C_{19+}	41.0	6.0	0
oxygen compounds	3.9	7.0	0
aromatics, % of gasoline		5	38.6

Fuel Cells

Catalysts, eg, noble metals on electrically conducting supports, are used at both the anode and cathode in a fuel cell (see Batteries and electric cells, primary; see also Hydrogen energy).

Environmental Control

Catalysts used for the abatement of noxious emissions (see Exhaust control, automotive; Exhaust control, industrial) were developed where the active component and substrate are supported on sturdy ceramic honeycomb structures, called monolithic supports. Platinum-group metal catalysts are used for nitric acid (qv) plant tail-gas cleanup. Platinum metals supported on SiO_2 , Al_2O_3 , and carbon are used as catalysts to eliminate organic fumes from air pollution and for fire safety (see Air pollution control methods). Hydrocarbon oxidation reactions are promoted via catalysts for emission control. Combustor systems are usually ceramic monolithic substrates coated with a catalytic agent. Catalysts are used in hydrogen sulfide conversion to sulfur (see Sulfur recovery).

About 60% of catalysts is used in the petroleum industry, and the remainder for major chemicals and chemical intermediates.

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H. Heinemann and J.J. Carberry, eds., *Catalysis Reviews*, Marcel Dekker, Inc., New York, 1968-present.

W.K. Hall, ed., *J. Catal.*, Academic Press, Inc., New York.

"Catalysts: a Chemical Market Poised for Growth," *Chem. Eng. News*, 19 (Dec. 5, 1983).

CATALYSIS, PHASE-TRANSFER

Phase-transfer catalysis (PTC) is a technique by which reactions between substances located in different phases are brought about or accelerated. It is also known as extractive alkylation, catalytic two-phase reaction, and preparative ion-pair extraction. Typically, one or more of the reactants is an organic liquid or solid dissolved in a nonpolar organic solvent and the coreactants are salts or alkali-metal hydroxides as solids or in aqueous solution. In principle, however, one reactant can be a gas, and the extracted species—normally an anion—can be a cation, a metal atom, or a neutral molecule. Catalysts used most extensively are quaternary ammonium or phosphonium salts, and crown ethers and cryptates.

There are two distinct classes of reactions formed under PTC conditions:

(1) Reactions without added bases, eg, displacement reactions such as $RX + Y^- \rightarrow RY + X^-$; oxidation reactions with oxidants such as $KMnO_4$, KO_2 , $K_3[Fe(CN)_6]$, $K_2Cr_2O_7$, $NaOCl$; as well as some reduction reactions.

(2) Reactions in the presence of inorganic bases (conc. aqueous solutions or finely ground solids of $NaOH$, KOH , K_2CO_3 , etc). These

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